

The Passivity of Co in Alkaline and Acidic Electrolytes Studied by X-ray Photoelectron Spectroscopy (XPS).

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Co is an important metal and alloy component for various tools in industry and implants in the human body due to its hardness and its excellent corrosion resistance. Co shows a complicated passive behaviour in alkaline and weakly acidic electrolytes. Low dissolution rates are caused by the presence of passive layers. With respect to the polarization curve of Co one may distinguish the potential range of primary and secondary passivity as shown for 0.1 M NaOH in Fig 1. In strongly acidic electrolytes the dissolution current densities are relatively high in the range of some mA/cm<sup>2</sup> and only a small plateau of secondary passivity appears immediately before the onset of oxygen evolution at 1.4 V (pH 2.2) as has been published already previously[1]. The separation of the potential range of primary and secondary passivity improves with increasing pH. The potential of the first anodic peak A1 and the onset of oxygen evolution shift by  $E = -0.059 \text{ V} / \text{pH}$  whereas A2 at the transition of the two passive ranges changes less.

The knowledge about the composition and structure of the protecting anodic layers of Co is rather poor. Therefore these passive layers have been investigated after well defined potentiostatic formation with systematic variation of the relevant parameters like time and potential and the composition of the electrolyte. The preparation of sputter cleaned samples occurs under the protection of purified argon with a subsequent transfer to the UHV of the XP-spectrometer within a closed system [2]. These conditions permit to start with oxide free specimens and allow oxide formation starting in the ms-time range and a transfer without any contamination. The evaluation of the XPS results occurs on the basis of well characterized standards [3]. Special care was taken to avoid the interference of disturbing signals as e.g. Auger signals. Quantitative XPS results include the cationic and anionic fractions of the layer i.e. the amount of hydroxide and oxide for the various possible oxidation states. Angular resolved XPS yields information of a possible multilayer structure.

The composition and thickness of the passive layer changes with potential in agreement with the polarization curve. In borate buffer pH 9.3 the thickness increases linearly with the potential in the primary passive range within ca 1 nm and takes a step to 4 nm at  $E = 0.75 \text{ V}$  [3]. In 0.1 M NaOH, pH 13, similar thicknesses are observed. In the active potential range negligible amounts of Co(II)-hydroxide are found. Co(OH)<sub>2</sub> covers the metal surface in the primary passive range which changes to Co(III)-oxide in the range of  $E = 0.2$  to  $0.4 \text{ V}$  with pure Co(III) at  $E > 0.4 \text{ V}$  (Fig. 2a). This formation of the Co(III) film coincides with the change of primary to secondary passivity with a characteristic sharp anodic peak in the polarization curve at  $0.3 \text{ V}$  (Fig. 1). Simultaneously a special peak at 530.3 eV contributes to the O1s-signal of the XP-spectrum which is interpreted by the formation of a spinell oxide at the metal surface. The O1s-signal proves the simultaneous presence of hydroxide, oxide, and spinell with the same concentration (Fig. 2b).

The passive layer formed at  $0.6 \text{ V}$  within the range of secondary passivity keeps its composition during stepping

the potential to more negative values till  $0.25 \text{ V}$  and changes from Co(III)-oxide to Co(II)-hydroxide at  $E \leq -0.2 \text{ V}$  as may be followed with the Co2p- and the O 1s-signal. Simultaneously with the change of an oxide to a hydroxide the spinell signal is disappearing. However, Co(OH)<sub>2</sub> is not reduced to metal at potentials as low as  $-0.8 \text{ V}$  within 5 min in 0.1 M NaOH.

The formation of the layer has been followed also in the time domain. During the first seconds Co(II) forms predominantly even in the range of secondary passivity but disappears gradually within several minutes, whereas Co(III) increases at the same extent. Simultaneously hydroxide is replaced by oxide although finally it is still present up to 30%. Again the formation of Co(III) is accompanied with the appearance of the spinell signal.

The application of XPS to the investigation of passivity of Co shows a complicated sequence of anodic oxides which are formed and may be reduced according to the electrode potential. Angular resolved XPS suggest an outer position of hydroxide and an inner position of oxide. Any further details to the composition and structure of the passive layer on Co are subject to our current investigations.

References:

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Fig. 1: Potentiodynamic polarization curve of Co in 0.1 M NaOH.

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Fig.2: Composition of passive layers formed in 0.1 M NaOH for 5 min as a function of potential, a) cationic fractions, b) anionic fractions of oxygen species including spinell (O<sup>2-</sup><sub>spin</sub>).